

Assistance Agreement Quarterly Report Summary: 11th Quarter

Date of Report: October 15, 2002

Agreement No: R82806301

Title: **Baltimore Supersite: Highly Time and Size Resolved Concentrations of Urban PM_{2.5} and its Constituents for Resolution of Sources and Immune Responses**

Investigators: **J. M. Ondov**, Department of Chemistry and Biochemistry, University of Maryland, College Park, MD; **T. J. Buckley**, School of Hygiene and Public Health, Johns-Hopkins University, Baltimore, MD; **P. K. Hopke**, Clarkson University, Potsdam, NY; **M. B. Parlange**, Johns-Hopkins University, Baltimore, MD; **W. F. Rogge**, Department of Civil and Environmental Engineering, Florida International University, Miami, Florida; **K. S. Squibb**, Department of Pathology, University of Maryland at Baltimore; and **A. S. Wexler**, University of California, Davis, CA

Institution: Department of Chemistry and Biochemistry, University of Maryland, College Park, MD

Research Category: Particulate Matter Supersites Program

Project Period: January 15, 2000 to December 31, 2003

Objectives of Research: Our primary objectives are to I) provide an extended, ultra high-quality multivariate data set, with unprecedented temporal resolution, designed to take maximum advantage of advanced new factor analysis and state-of-the-art multivariate statistical techniques; ii) provide important information on the potential for health effects of particles from specific sources and generic types of sources, iii) provide large quantities of well characterized urban PM for retrospective chemical, physical, biologic analyses and toxicological testing, iv) provide sorely needed data on the sources and nature of organic aerosol presently unavailable for the region, v) provide support to existing exposure and epidemiologic studies to achieve enhanced evaluation of health outcome-pollutant and -source relationships, and vi) test the specific hypothesis listed in our proposal.

ACTIVITIES

During the 11th report period the following activities were performed.

1. Continued operation of the Ponca St. Site with full instrumentation
2. Presentations were made at the Fall AAAR meeting in Charlotte
3. Quality assurance, database loading, and preparations for transferring data to the NARSTO

data base are in progress.

4. We are preparing for our final intensive sampling campaign

Additional information on these activities is presented below..

STATUS

Supersite Instrument operation

We continue to operate all instruments at Ponca St., our main Supersite. These are as follows:

1. RSMSIII - single particle mass spectrometer
2. High-Frequency Aerosol Slurry Samplers - Separate instruments are deployed for metals and cytokine assays, both at 30 min time resolution.
3. Scanning Mobility Particle Sizer (SMPS) - 9 to 450 nm, every 5 minutes
4. Aerodynamic Particle Sizer (APS) - 500 nm to 20 μ m, every 5 minutes
5. 30-degree TEOM for 30 min aerosol mass concentrations
6. R&P 8400N Nitrate Monitor - 10 min particulate nitrate
7. Harvard/Edgerton Sulfate instrument - 30 min sulfate concentrations
8. Sunset Labs EC/OC - hourly
9. Meteorological station: Wind speed (two heights) and direction, Temperature, Relative Humidity, solar insolation, and rain.
10. Lidar (1 in 6 days, daily during the July Intensive campaign; lidar measurements were made at Homewood on April 16, 24, 30, May 6, 14, 16, 22; June 12, 23, and 29. Daily measurements were made at Ponca St. in July.
11. 3-D sonic anemometer has been restored to the site
12. Speciation and FRM sampling - daily during July intensive, 1 in 3 days otherwise.
13. UM Fine Particle Sampler, every other day, using the SEAS PM inlet.
14. Two Radiance Research Integrating Nephelometers

In addition, the Maryland Department of Environment (MDE) is operating the following:

15. VOC by online GC
16. Ozone, NO, NO₂, and CO
17. Speciation and FRM sampling at Essex (1 in 3 days)

RSMSIII. Single particle mass spectra were obtained throughout the third quarter with the RSMS-3 instrument. Single particle measurements were performed in the following manner: a complete sample cycle was performed every two hours except for maintenance and repair periods. During an individual sample cycle, measurements were made sequentially for 9 particle sizes between 45 and 1240 nm diameter (aerodynamic). For each size, the measurement period ended after 10 minutes or the acquisition of 30 particle mass spectra, whichever came first. Typically, 30-40 minutes were required to cycle through the 9 particle sizes for the ambient particle concentrations present during this time period.

Maximum number of particle hits: 240 particles/interval or 2880 particles/day

Typical number of particle hits: 1500-2200 particles/day

Total particle hits between 3/20/02 and 9/30/02: 256,000

Fraction of time lost to maintenance and repair during third quarter: <10%

We have estimated the detection efficiency (D) of the mass spectrometer, defined as the fraction of particles entering the inlet that are ablated and detected, can be estimated from the particle concentration measured with the mass spectrometer divided by the particle concentration measured with a scanning mobility particle sizer:

$$D = \frac{[dN/d(\log d_p)]_{SMS}}{[dN/d(\log d_p)]_{SMPS}} \quad (1)$$

The particle concentration measured with the mass spectrometer is given by:

$$[dN/d(\log d_p)]_{SMS} = \frac{N/tV}{\log \left(\frac{d_m}{\sigma_g} \right)^2} \quad (2)$$

where N is the total number of particles detected during time interval t , V is the volume flow rate of aerosol into the mass spectrometer, d_m is the median diameter transmitted by the inlet, σ_g is the geometric standard deviation of the inlet transmission function, and $\log (d_m/\sigma_g)^2$ represents the width of the transmission function between 16% and 84% of the size distribution. The number concentration of particles having a particular chemical composition is given by:

$$[dN/d(\log d_p)]_{apparent} = \frac{N/tV}{D \log \left(\frac{d_m}{\sigma_g} \right)^2} \quad (3)$$

where N is the total number of particles of a given composition that are detected during time interval t , and the other parameters are as above. The total particle concentration is then determined through integration:

$$N_p = \int [dN/d(\log d_p)] d \log d_p \quad (4)$$

Now that we have estimated the detection efficiency (D), these equations can be used to determine the size distribution, number concentration, time/wind dependencies of particles containing specific chemical components. We are beginning to analyze our data using this approach.

LIDAR. Table 1. Days of operation of the JHU lidar system at the Ponca St. site during July 15 to September 15, 2002. Time period July 15 - October 15

Table 1. Days of operation of the JHU lidar system at the Ponca St. site during July 15 to October 15, 2002. White fields indicates that lidar data is available. The lidar system is broken since September 12 (blue field).

The lidar system could not be operated when it was raining. Data were taken at daytime only in order to comply with FAA regulations. The duration of an individual lidar scan (vertically upward pointing) was between 30 minutes to 1 hour. In some cases the lidar scans had to be stopped due to heavy air traffic or because of rain.

The determination of the ABL top for each scan of 30 minutes to one hour duration is being continued in order to obtain a

comprehensive data set. The

resulting mean boundary layer heights and their standard deviation are combined to yield a time series of ABL height and are then stored in the database.

JULY_02	AUGUST_02	SEPTEMBER_02	OCTOBER_02
	1	1	1
	2	2	2
	3	3	3
	4	4	4
	5	5	5
	6	6	6
	7	7	7
	8	8	8
	9	9	9
	10	10	10
	11	11	11
	12	12	12
	13	13	13
	14	14	14
15	15	15	15
16	16	16	
17	17	17	
18	18	18	
19 (bio)	19	19	
20	20	20	
21	21	21	
22	22	22	
23	23	23	
24 (bio)	24	24	
25 (bio)	25	25	
26	26	26	
27	27	27	
28	28	28	
29	29	29	
30	30	30	
31	31		

Lidar data (Figure 1) for April 11th and August 14th were presented at the AAAR meeting in Charlotte. These days represent Spring (low solar insolation, low early morning winds and low early morning mixing height, and high morning RH) and Summer (higher solar insolation, high afternoon mixing height, and high morning RH). As discussed below PM episodes were examined for April and July/August dates.

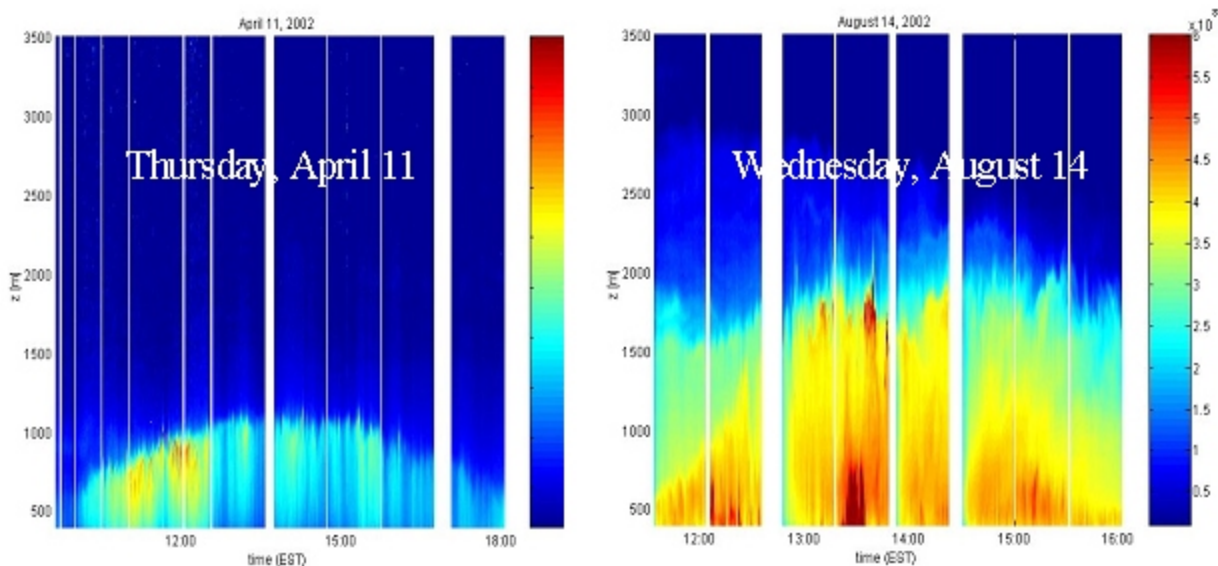


Figure 1. Relative concentrations of particles as a function of height and time of day during typical Spring and Summer days were developed with the JHU Lidar system.

November Intensive Sampling Campaign

In addition to the instruments described above, we are in the process of installing a second Micro-Orifice Impactor and a second University of Maryland Fine Particle Sampler. These will be run in parallel with the existing instruments to provide co-collected samples for metals and cytokine assays during the November campaign. Colleagues from the University of Maryland Chesapeake Biological Laboratory will again collect aerosol particles in 24 - hr filter and Berner Impactor samplers for PAH analyses to compliment the our time-resolved measurements.

PROGRESS SUMMARY/ACCOMPLISHMENTS

Some Highlights from the Fall AAAR Meeting

Comparison of Semicontinuous and 24-hr Nitrate Speciation Measurements (Clarkson University).

The Baltimore Supersite measurements at Clifton Park produce both semi-continuous sulfate and nitrate data with R&P 8400n and s and the 24-hr integrated filtered data with the Metone SASS speciation network sampler. It is useful to relate (or calibrate) these two kind of measurements, which can indicate 1) if there is an equal weight of 24 hourly value needed to accurately reproduce the 24-hr integrated values, 2) the possibility to estimate the 24-hr integrated value using the 24 hourly values, and 3) the deficiencies and differences between two measurements. We have begun with the nitrate concentration data from Baltimore Supersite Clifton Park site during the period of 6/28/01 to 9/15/01. The data preprocessing was as follows: 1) take the mean value of six samples in one hour as the hourly average concentration, 2) delete the days whose numbers of the missing hourly values are more than 10, and 3) replace the rest hourly missing values with the mean value of their neighbors. This process leaves 34 pairs of 24

hourly concentrations and the corresponding integrated filtered value. Among various calibration methods, we compared the least square regression (LSR), principal components regression (PCR), and partial least square regression (PLSR). Leave one out (LOO) cross validation was applied to measure the property of each calibration method.

The experimental results can be briefly described as 1) The training set accuracy increases with the number of PCs or PLSCs, while the prediction accuracy initially increases and then decreases with the number of PCs or PLSCs, and in general, we need to find a proper number of PCs or PLSCs. For example, the proper extracted components' numbers for 'group 1' are 10 for PCR and 6 for PLSR respectively. 2) PLSR produces better fits (at least on the training set) than PCR with the same number of extracted components, 3) PCR or PLSR will be degraded to LSR when the number of PCs or PLSCs equals the number of independent variables, 4) The weights of 24 hourly values for reproducing the 24-hr integrated values are different. The following conclusions can be made: 1) There is a relationship between the semi-continuous measured concentration and the integrated 24-hr filter value, and the linear methods can be used to build this relationship, 2) Among the linear calibration methods, PLSR and PCR produce better fits to the 24-hour integrated values than LSR and PLSR is better than PCR. In addition, if adequate data can be obtained, this relationship can help to get more accurate weights of 24 hourly concentrations to estimate the 24-hour integrated sample data, to identify bad data (outliers), to compare the differences between two measurements, and to study the influence of conditional factors (eg. seasonal factor).

Characterization of High PM Episodes. Speciation data were examined to understand the nature of high PM episodes observed in April and July 5 - August 15, 2002, i.e., periods representing lower sunlight and lower mixing heights typically observed in spring, with periods of high sunlight and higher mixing heights observed in summer. A total of five periods wherein PM_{2.5} mass concentrations measured with the 30° TEOM at Ponca St. exceeded 40 µg/m³ were examined. Two episodes occurred in data examined for April, i.e., April 16th and 17th. As shown in Figure 1, PM mass peaked between 6:00 and 9:00 AM, i.e., during the morning rush periods, in both episodes, however the second episode was characterized by a mass excursion occurring around 02:30 AM. Both Organic carbon and Elemental Carbon were substantial fractions of both episodes, so much so, that TEOM mass concentrations were highly correlated with OC and not sulfate. Total Particle number concentrations (diameters >10 nm) also peaked during the onset of these periods and corresponded to peaks in NO_x emissions. On both days, RH exceeded 80% during the early morning hours and particulate nitrate contributions to PM mass concentrations were observed to be substantial (15%) at 9:00 AM. We believe that the particulate nitrate peaks represent scavenging of Nitric acid formed later from rush-hour NO_x emissions, which were scavenged by the still wet aerosol particles. One interesting observation is that the high nitrate events were very well correlated with the total concentrations of particles >0.5 µm as measured with the TSI Aerodynamic Particle Sizer (APS). On the 17th, elemental and organic contributions to PM mass concentrations were also substantial in late morning, i.e., 15 and 20% respectively and seemed to drive the late morning mass peak. During both periods, OC:EC ratios were approximately 2, suggesting motor vehicles sources. This ratio increased to

between 6 and 12 during the afternoons.

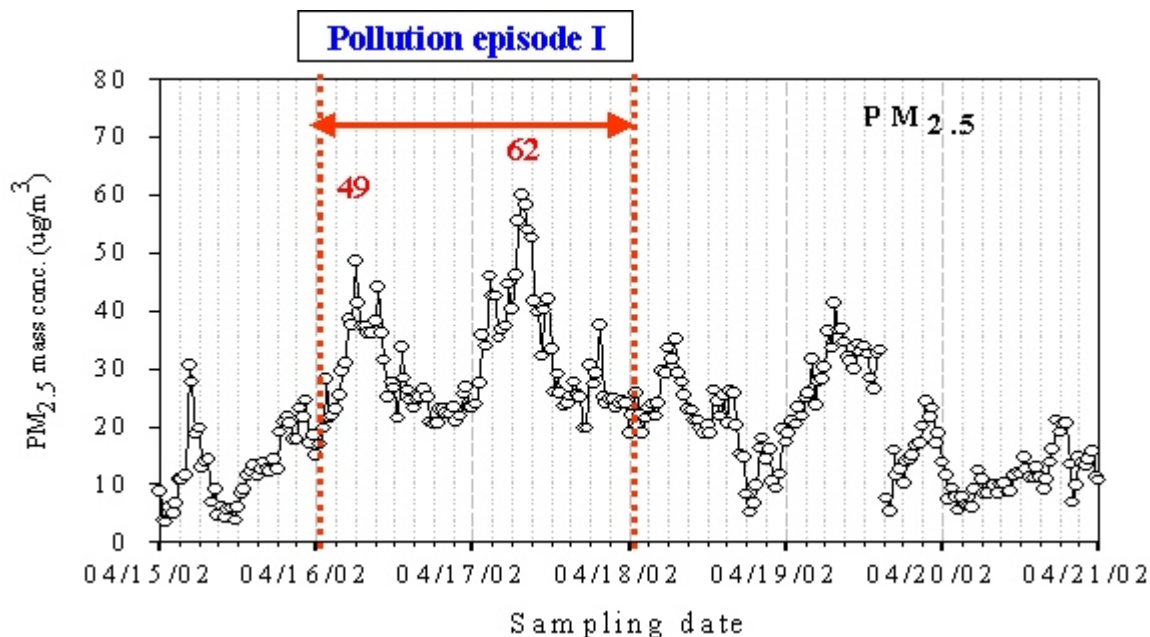


Figure 2. High PM_{2.5} concentrations were observed during a 2-day period in April. These were heavily influenced by EC, OC, and Nitrate, which accounted for 60% of the PM_{2.5} mass during peak PM concentrations in this period.

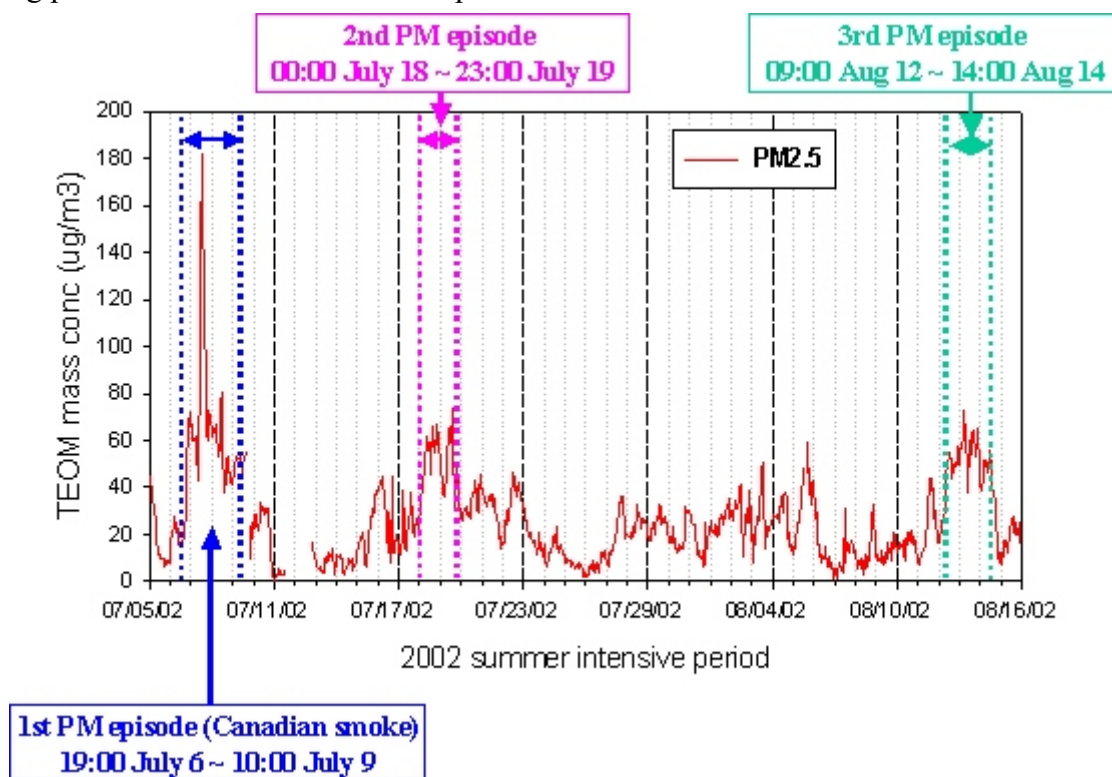


Figure 3. Summer PM_{2.5} episodes were typically dominated by Sulfate, with the exception of the Canadian Smoke event, which occurred during the week of July 5th.

In contrast, PM_{2.5} events recorded in Summer (Figure 3) were largely explained by sulfate, with the exception of the period July 6 through July 9th, during which the northeastern US was exposed to smoke from Canadian forest fires.

Cytokine Assays. Cytokine assays provide a metric of Immune Inflammatory response. Cytokine production (and inhibition of production) has been demonstrated invitro and invivo for several transition metals, which might, in part, explain inflammatory response induced by exposure to PM. Cytokine responses were successfully measured in 30-min aerosol slurry samples collected at FMC (Figure 4.). As shown previously, dose response curve were linear.

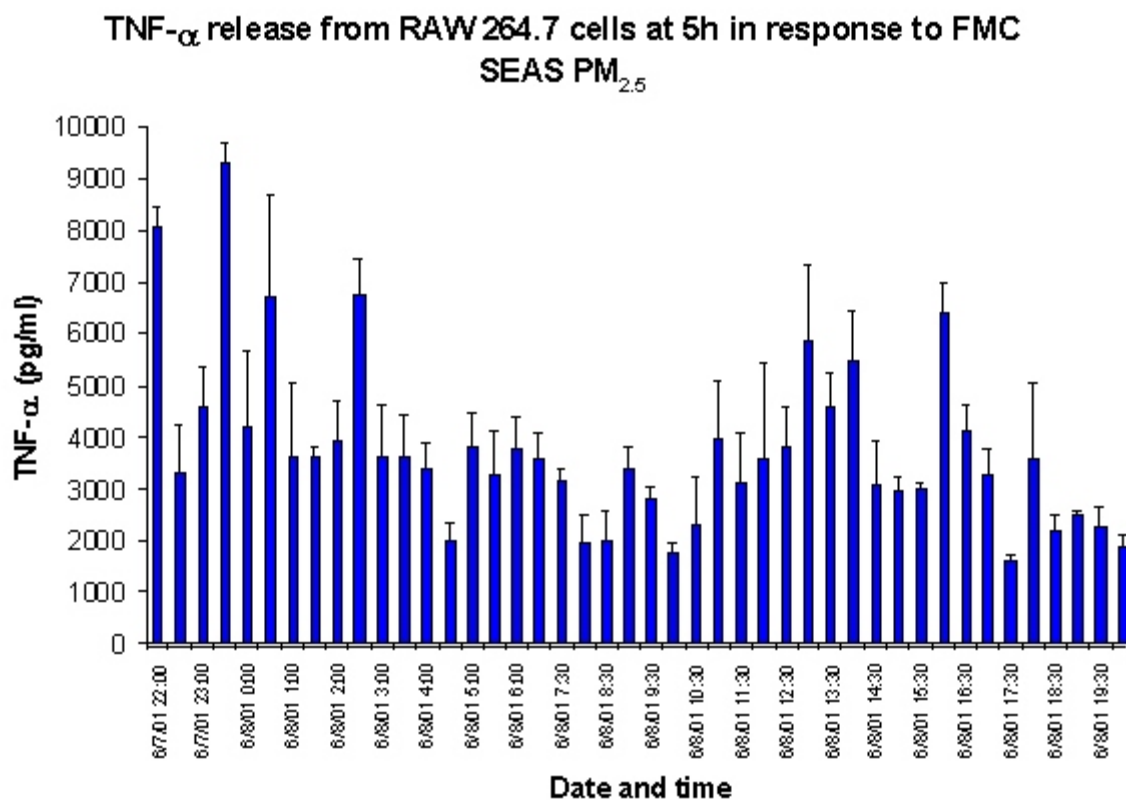


Figure 4. Cytokine TNF- α concentrations induced by exposure of RAW cells to particles collected in sequential 30-min intervals at the FMC site.

Three-hr Organic Compound Data

Within Baltimore, the composition and concentration of organic aerosol is only known to a limited extent. Consequently, the lack of suitable organic PM_{2.5} data has so far precluded refined source/receptor reconciliation. The current ongoing study will provide a comprehensive data set that includes summer as well as winter sampling. Here, for the very first time, ambient concentrations of organic compounds associated with PM_{2.5} are determined on a three hour interval for a total of

28 days during two intensive periods: summer and winter of 2002. This enhancement in time resolution will provide the opportunity to investigate the dynamics of organic PM_{2.5} ambient concentrations, and is expected to allow a finer determination of many source contributions.

PM_{2.5} was collected using a specially designed sampling system that allows to collect organic matter on filter and PUF substrates. The sampling system has five separate sampling channels connected to one PM_{2.5} inlet and is operated in a sequential mode. Individual sampling time is three hours and the nominal flow rate is 600 l/min. Filter and PUF samples separately, are solvent extracted and analyzed by GC/MS for more than 100 organic compounds, including: normal and branched-alkanes, alkylcyclohexanes, n-alkanoic acids, n-alkenoic acids, dicarboxylic acids, aromatic acids, resin acids, sterols, hopanes, steranes, PAHs, oxy-PAHs, sugars, thiazoles, secondary oxidation products and others.

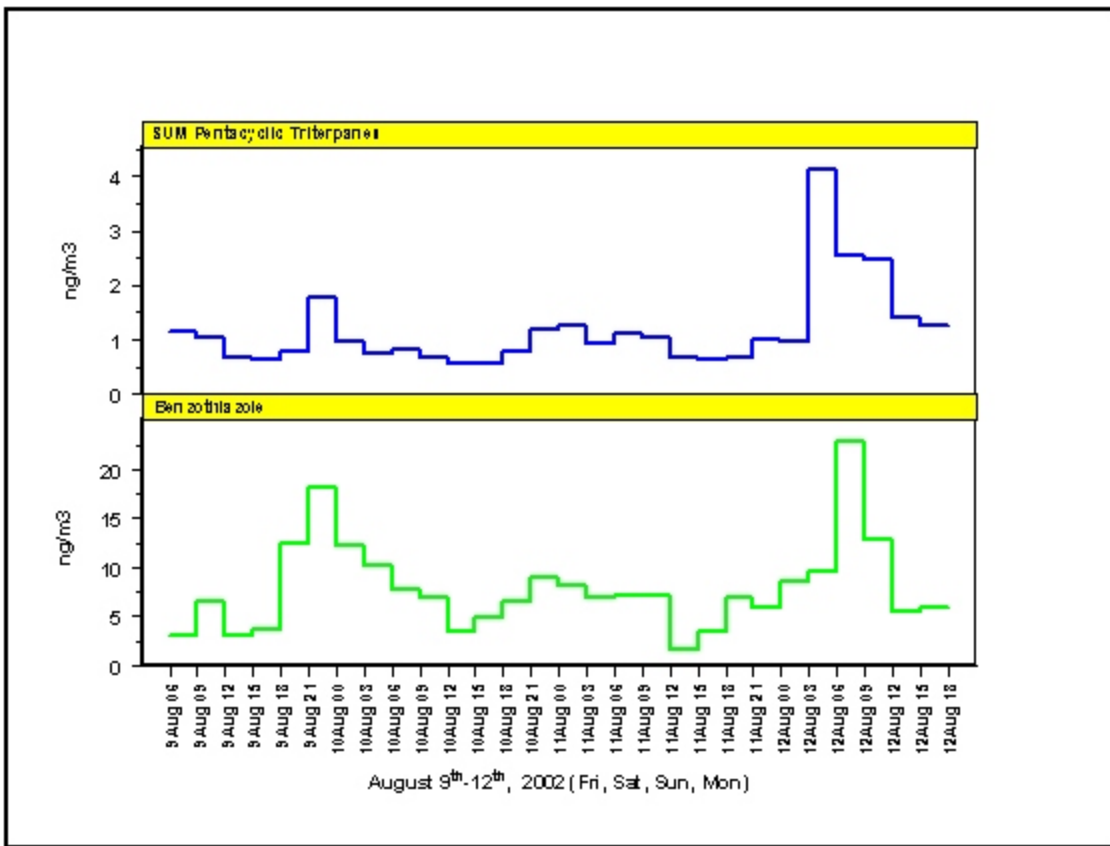


Figure 5. Concentrations of pentacyclic triterpanes and benzthiazoles in sequential 3-hr samples collected at the Baltimore Supersite in August, 2002.

The intensive summer sampling campaign for organic PM_{2.5} began on July 14, 2002 and ended on August 12, 2002. Some of the results of a limited set of ambient organic PM_{2.5} data covering three consecutive days are presented below. Compounds detected included Pentacyclic triterpanes (hopanes) emitted mainly from motor vehicles. These show a concentration pattern similar to that

of benzothiazoles, a unique marker for tire wear particles which were also detected. PAHs and oxy-PAHs follow the same trend. Cholesterol concentrations are higher at typical times of food preparation. Alkenoic acids follow the same trend. Levoglucosan, released by the combustion of wood, wood products and biomass in general, shows a concentration pattern that follows that of dehydroabietic acid, a marker for soft wood burning.

Baltimore Supersite Relational Database (BSSRDB)

The BSSRDB now contains all data collected prior to August 30th, 2002 except for Single Particle MS, speciation and FRM monitor, SEAS elemental analysis, and cytokine data. Complete meta data have been assembled for our instruments and is available on the BSSDB Server machine (FATBOY). These data are being used to complete NARSTO templates for transfer of data to the NARSTO archive.

Several sets of data have been transferred to the EPA Supersites Relational Data FTP site.

Data Flagging. We continue implementation of flagging BSSDB data using two types of procedures. The first is an instrument parameter file processor, which scans the parameters captured in the data stream of each of our instruments and flags the data as good, questionable, correctable, questionable and correctable, or bad, based on instrument status codes, expected data range, and criteria specific to each instrument. For example, when the values of the reaction cell Pressure deviate from 5 inches of Hg, the correctable flag is assigned. When the sampling cell compartment temperature differs from the ambient outside temperature by more than 4°C, the correctable flag is also set, in anticipation of future corrections factors to be applied. The second is a web based application that permits flagging of data based on operator log information. The instrument operator provides a table of date/times of non “good” data or the unique data ID number. The information in the table are then loaded to the web-based operator flagging application by the data manager. These applications and protocols permit rapid flagging of data and minimization of flagging errors. An improved operator’s log flagging application has been coded and made web accessible, during this progress period.

Publications/Presentations/meetings

Supersites Instrumentation Meeting, Las Vegas, June 2002:

1. Ondov, J. M., Ondov, D. J. (2002) Las Vegas - Evaluation of SEAS technology for Routine Application in the EPA Speciation Program. Presented at the EPA meeting on Supersites Instrumentation, June 12-13, Las Vegas.

AGS Meeting, San Francisco, December, 2002

2. Adam, M., Pahlow, M., Ondov, J., Thomas, M., Parlange, M. (2002) Atmospheric boundary layer extinction coefficient from the 2001/2002 Baltimore PM Supersite experiments. To be presented at the Fall meeting of the American Geophysical Society, Dec. 6-7, San Francisco.

AAAR Meeting, Charlotte, October, 2002

3. SONG, X.-H., Hopke, P. K., Paatero, P., Ondov, J. M., Kidwell, C. B. (2002). Source Identification by a Multilinear Receptor Model Using Highly Time Resolved Chemical Composition and Wind Data. To be presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
4. Ondov, J. M. (2002) Highly Time and Size Resolved Concentrations of Urban Pm_{2.5} and its Constituents for Resolution of Sources and Immune Responses: Highlights of Results from the Baltimore Supersite Project." To be presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
5. Harrison, D., Nair, N., Park, S. S., Pancras, J. P., Gazula, S., Ondov, J. M. (2002) Resolution of a Municipal Diesel Emission Component at the Baltimore Supersite from Highly Time- and Compositionally-resolved Aerosol and Gas Measurements To be presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
6. Mitkus R., Squibb¹, K., Powell, J., Catino, D. H., Ondov, J. M. (2002). In Vitro Assay of the Biological Activity of Pm_{2.5} and its Components Collected by a High Frequency Aerosol Sampler at an Urban Supersite. To be presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
7. Park, S. S., Pancras, P., Chang, Y. C., Catino, D. H., Gazula, S., Ondov, J. M. Seung S. Park, Patrick Pancras, Yu Chen Chang, Dawn H. Cation, and S. (2002) Investigation of Sources with Highly Time-resolved Aerosol at the Baltimore Supersite Using Positive Matrix Factorization To be presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
8. Pancras, J. P., Gazula, S., Park, S. S., Ondov, J. M., Stevens, R. K. (2002) Elemental and Inorganic Analysis of Highly-time-resolved Aerosol Constituents in the Tampa Bay Regional Atmospheric Chemistry Experiment (BRACE) To be presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.
9. Park, S. S., Pancras, J. P., Gazula, S., Ondov, J. M. (2002) Sources of Elemental Aerosol Constituents in Pittsburgh Using Positive Matrix Factorization of Highly Time-resolved Data To be presented at the American Association of Aerosol Research meeting, 21st Annual AAAR Conference October 7-11, Charlotte.

Future Activities.

1. We will continue to hold weekly PI teleconferences as needed.
2. We will conduct a 30-day intensive sampling campaign in November 2002.
3. We are in the process of preparing several abstracts for the March 2003 AAAR PM meeting.
4. Samples are being selected for retrospective analyses. DRUM impactor samples collected during July, 2002 are to be analyzed during the week of November 20, 2002. Elemental analyses and Cytokine assays for 30-min slurry samples are being scheduled.

5. We will complete data flagging and Level II QA activities and transfer data to NARSTO, anticipated completion: before Jan 1, 2003.

